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TRANSMITTAL LETTER TO THE UNITED STATES							
DESIGNATED/ELECTED OFFICE (DO/EO/US)							
CONCERNING A FILING UND							
ATTORNEY DOCKET NUMBER IN-5495	U.S. APP 10 910/ 18 (K 9 2 5 7 15)						
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED					
PCT/EP00/00779	1 February 2000 (01.02.00)	3. February 1999 (03.02.99)					
TITLE OF INVENTION: POLYURETHAN	E AND ITS USE IN AQUEOUS PAINTIN	G PLASTIC					
APPLICATION(S) FOR DO/EO/US: Stephan SCHWARTE and Michael HARTUNG							
Applicant herewith submits to the Unit information:	ted States Designated/Elected Office (DO/E	EO/US) the following items and other					
1. X This is a FIRST submission of	f items concerning a filing under 35 U.S.C. 37	71.					
2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.							
3. This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1). A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date							
priority date  A copy of the International Application as filed (35 U.S.C. 371(c)(2))  a							
6.17 X A translation of the International Application into English (35 U.S.C. 371(C)(2)).							
7. X Amendment to the claims of the International Application under PCT Article 19 (35 U.S.C.371(c)(3)) a. arrivansmitted herewith (reguired only if not transmitted by the International Bureau). b. have been transmitted by the International Bureau. c. have not been made; however, the time limit for making such amendments has NOT expired. X have not been made and will not be made							
(m)	ents to the claims under PCT Article 19 (35 U. inventor(s) (35 U.S.C. 371(c)(4)).	S.C. 371(c)(3)).					
_		ort under DCT Article 20					
10. A translation of the annex to the International Preliminary Examination Report under PCT Article 36  Items 11. to 16. below concern other document(s) or information included:							
11. X An Information Disclosure Sta	atement under 37 CFR 1.97 and 1.98.						
12. An assignment document for	recording. A separate cover sheet in complia	nce with 37 CFR 3.28 and 3.31 is included					
13. X A FIRST preliminary amendm A SECOND or SUBSEQUENT	ent. Г preliminary amendment.						
14. A substitute specification.							
15. A Change of power of attorne	y and/or address letter.						
16. X Other items or information: A copy of the cover sheet from the PCT .	Published Application						
I hereby certify that the attached correspon Post Office to Addressee" Mailing Label No. Ef June 26, 2001.	dence is being deposited with the United States Possesses addressed to the Assistant Commis	ostal Service in an envelope as "Express Mail ssioner for Patents, Washington, D.C. 20231 on					
Muy Su Marjorie Ellis	<u>~`</u>	-8-					

U.S. APPLICATION NO	(If province 17 C.E.R. 1.50	INTERNATIONAL APPLICAT	TION NO.	ATTORNEY'S DO	CKET NUMBER		
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17. X The following				CALCULATIO	NS   PTO USE ONL		
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accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +							
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				Charged	\$860.00		
a. A check in the amount of \$ to cover the above fees is enclosed.							
b. X Please charge my Deposit Account No. 23-3425 in the amount of \$860.00 to cover the above fees							
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The Commission of the Commissi							
c. X The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any							
overpayment to Deposit Account No. <u>23-3425</u> . A triplicate copy of this sheet is enclosed.  NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR							
1.137(a) or (b)) must be filed and granted to restore the application to pending status.							
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Southfield, Michigan 4	18034-2442	Name		_			
(248) 948-2355 42,906							
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PATENT (Practitioner's Docket No. IN-5495)

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Stephan SCHWARTE Michael HARTUNG

Serial No.: This application is a National Phase of Patent Application PCT/EP00/00779

filed 1 February 2000.

Filed: June 26, 2001

For: POLYURETHANE AND ITS USE IN AQUEOUS PAINTING PLASTIC

Group Art Unit: Not Assigned

Examiner: Not Assigned

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee" Mailing Label No. <u>EF325208526US</u> addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231 on June 26, 2001.

Marjorie Ellis

# PRELIMINARY AMENDMENT UNDER 37 CFR § 1.115

Commissioner for Patents Washington, D.C. 20231

Sir:

This preliminary amendment is submitted with the application for entry into the U.S. National Phase under Chapter II. This application is based on PCT/EP00/00779 filed on 1 February 2000.

In connection with the filing of this National Phase application, please make the following preliminary amendments.

#### IN THE CLAIMS:

Please cancel claim 7 without prejudice or disclaimer.

Please substitute claims 1-6 and 8 as follows.

- 1. (Amended) A polyurethane comprising a reaction product of
  - (a1) at least one polyesterpolyol having a number average molecular weight Mn of from 1,000 to 4,000, an acid number of from 0 to 15, and an OH number of from 35 to 150, wherein the polyesterpolyol is an esterification product of at least one of an acyclic aliphatic dicarboxylic acid, an anhydride of an acyclic aliphatic dicarboxylic acid, an esterifiable derivative of an acyclic aliphatic dicarboxylic acid, a cycloaliphatic dicarboxylic acid, an anhydride of a cycloaliphatic dicarboxylic acid, and an esterifiable derivative of a cycloaliphatic dicarboxylic acid.
  - (a2) a mixture of at least one diol and one triol,
  - (a3) at least one compound containing at least two isocyanate-reactive functional groups and at least one functional group capable of forming anions, and
  - (a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate,

wherein the polyurethane has a number average molecular weight  $M_n$  of from 3,000 to 50,000 and an acid number of from 10 to 35, with the proviso that

- (i) in the mixture (a2), the diols and triols are in a molar ratio of from 2:1 to 13:1,
- the molar ratio of the polyesterpolyols (al) to the mixture (a2) is from 4.5:1 to 1:1, and
- in the mixture (a4), the acyclic aliphatic and cycloaliphatic diisocyanates are in a molar ratio of from 1:0.16 to 1:6;

wherein the polyurethane is an isocyanato-containing prepolymer that is then chain extended with a polyfunctional amine or amino alcohol.

- 2. (Amended) A polyurethane dispersion comprising
  - (A) at least one polyurethane as claimed in claim 1
  - (B) in dispersion in an aqueous medium comprising water.

- 3. (Amended) The polyurethane as claimed in claim 1, wherein the polyurethane is used to make at least one of a plastics finish, an aqueous coating material, and an aqueous coating material for plastic finishing.
- 4. (Amended) The polyurethane dispersion as claimed in claim 2, wherein the polyurethane dispersion is used to make at least one of a plastics finish, an aqueous coating material, and an aqueous coating material for plastic finishing.
- 5. (Amended) The polyurethane as claimed in claim 1 in an aqueous coating material, said aqueous coating material further comprising at least one of color pigments, effect pigments, and coatings additives.
- 6. (Amended) The polyurethane dispersion as claimed in claim 2 in an aqueous coating material, said aqueous coating material further comprising at least one of color pigments, effect pigments, and coatings additives.
- 8. (Amended) A plastics finish that is obtained by the steps of
  - (I) applying a two component water based primer and curing it to give a primer coat,
  - applying to the primer coat as a basecoat, an aqueous coating material comprising the polyurethane of claim 1,
  - (III) applying a two component clearcoat material wet on wet, and
  - (IV) curing the resultant basecoat and clearcoat films.

Please insert the following new claims 9-11:

- 9. (New) A plastics finish that is obtained by the steps of
  - (I) applying a two component water based primer and curing it to give a primer coat,
  - applying to the primer coat as a basecoat, an aqueous coating material comprising the polyurethane dispersion of claim 2,
  - (III) applying a two component clearcoat material wet on wet, and
  - (IV) curing the resultant basecoat and clearcoat films.
- 10. (New) The polyurethane of claim 1, wherein the polyurethane is neutralized.
- 11. (New) The polyurethane dispersion of claim 2, wherein the polyurethane is neutralized.

### IN THE ABSTRACT

Please substitute the following abstract, which has been amended to be less than 150 words in length.

#### ABSTRACT

A polyurethane which has a number average molecular weight  $M_n$  of from 3,000 to 50,000 and an acid number of from 10 to 35 and is preparable by reacting

- (al) at least one polyesterpolyol having a number average molecular weight M<sub>n</sub> of from 1,000 to 4,000, an acid number of from 0 to 15, and an OH number of from 35 to 150, based on acyclic aliphatic and cycloaliphatic dicarboxylic acids,
- (a2) a mixture of at least one diol and one triol.
- (a3) at least one compound containing at least two isocyanate-reactive functional groups and at least one functional group capable of forming anions, and
- (a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate,

to give an isocyanato-containing prepolymer that is then chain extended with a polyfunctional amine or amino alcohol and, if desired, is neutralized.

## Version with Markings to Show Changes Made

- (Amended) A polyurethane <u>comprising a reaction product of [which has a number average molecular weight Mn of from 3,000 to 50,000 and an acid number of from 10 to 35 and is preparable by reacting]</u>
  - (a1) at least one polyesterpolyol having a number average molecular weight M<sub>n</sub> of from 1,000 to 4,000, an acid number of from 0 to 15, and an OH number of from 35 to 150, [based on acyclic aliphatic and cyclo-aliphatic dicarboxylic acids] wherein the polyesterpolyol is an esterification product of at least one of an acyclic aliphatic dicarboxylic acid, an anhydride of an acyclic aliphatic dicarboxylic acid, an esterifiable derivative of an acyclic aliphatic dicarboxylic acid, an anhydride of a cycloaliphatic dicarboxylic acid, and an esterifiable derivative of a cycloaliphatic dicarboxylic acid, and an esterifiable derivative of a cycloaliphatic dicarboxylic acid,
  - (a2) a mixture of at least one diol and one triol.
  - (a3) at least one compound containing at least two isocyanate-reactive functional groups [(a31)] and at least one functional group [(a32)] capable of forming anions, and
  - (a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate,

wherein the polyurethane has a number average molecular weight  $M_n$  of from 3,000 to 50,000 and an acid number of from 10 to 35, with the proviso that

- (i) in the mixture (a2), the diols and triols are in a molar ratio of from 2:1 to 13:1,
- (ii) the molar ratio of the polyesterpolyols (al) to the mixture (a2) is from 4.5:1 to 1:1, and
- (iii) in the mixture (a4), the acyclic aliphatic and cycloaliphatic diisocyanates are in a molar ratio of from 1:0.16 to 1:6;

[to give] wherein the polyurethane is an isocyanato-containing prepolymer [which] that is then chain extended with a polyfunctional amine or amino alcohol[ and, if desired, is neutralized].

- 2. (Amended) A polyurethane dispersion comprising
  - (A) at least one polyurethane as claimed in claim 1
  - (B) in dispersion in an aqueous medium comprising water.
- 3. (Amended) The [use of the] polyurethane as claimed in claim 1, wherein the polyurethane is used to make at least one of a plastics finish, an aqueous coating material, and an aqueous coating material for plastic finishing [or the polyurethane dispersion as claimed in claim 2 in plastics finishing].
- 4. (Amended) The [use of the polyurethane as claimed in claim 1 or the] polyurethane dispersion as claimed in claim 2, wherein the polyurethane dispersion is used to make at least one of a plastics finish, an aqueous coating material, and an aqueous coating material for plastic finishing [in an aqueous coating material].
- 5. (Amended) The [use of the] polyurethane as claimed in claim 1 [or the polyurethane dispersion as claimed in claim 2] in an aqueous coating material, said aqueous coating material further comprising at least one of color [and/or effect] pigments, effect pigments, [(C)] and coatings additives.
- 6. (Amended) The [use of the polyurethane as claimed in claim 1 or the] polyurethane dispersion as claimed in claim 2 in an aqueous coating material, said <u>aqueous coating</u> material further comprising <u>at least one of color pigments</u>, <u>effect pigments</u>, and coatings additives [(D)].
- 8. (Amended) [The use of the polyurethane as claimed in claim 1 or the polyurethane dispersion as claimed in claim 2 in plastics finishing, wherein the]  $\underline{\mathbf{A}}$  plastics finish  $\underline{\mathbf{that}}$  is obtained by the steps of
  - (I) applying a two component water based primer and curing it to give a primer coat,
  - applying to the primer coat as a basecoat, an aqueous coating material comprising the polyurethane of claim 1 [to the primer coat],

- (III) applying a two component clearcoat material wet on wet, and
- (IV) curing the resultant basecoat [/] and clearcoat films.
- 9. (New) A plastics finish that is obtained by the steps of
  - (I) applying a two component water based primer and curing it to give a primer coat,
  - applying to the primer coat as a basecoat, an aqueous coating material comprising the polyurethane dispersion of claim 2,
  - (III) applying a two component clearcoat material wet on wet, and
  - (IV) curing the resultant basecoat and clearcoat films.
- 10. (New) The polyurethane of claim 1, wherein the polyurethane is neutralized.
- 11. (New) The polyurethane dispersion of claim 2, wherein the polyurethane is neutralized.

#### ABSTRACT

A polyurethane which has a number average molecular weight  $M_n$  of from 3,000 to 50,000 and an acid number of from 10 to 35 and is preparable by reacting

- (al) at least one polyesterpolyol having a number average molecular weight M<sub>n</sub> of from 1,000 to 4,000, an acid number of from 0 to 15, and an OH number of from 35 to 150, based on acyclic aliphatic and cycloaliphatic dicarboxylic acids,
- (a2) a mixture of at least one diol and one triol,
- (a3) at least one compound containing at least two isocyanate-reactive functional groups [(a31)] and at least one functional group [(a32)] capable of forming anions, and
- (a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate,

[with the proviso that

- (i) in the mixture (a2) the diols and triols are in a molar ratio of from 2:1 to 13:1,
- (ii) the molar ratio of the polyesterpolyols (al) to the mixture (a2) is from 4.5:1 to 1:1, and
- (iii) in the mixture (a4) the acyclic aliphatic and cycloaliphatic diisocyanates are in a molar ratio of from 1:0.16 to 1:6;

to give an isocyanato-containing prepolymer that is then chain extended with a polyfunctional amine or amino alcohol and, if desired, is neutralized [; and the use of the polyurethane for preparing polyurethane dispersions and coating materials for the finishing of plastics].

## REMARKS

Upon entry of the present amendment, claims 1-6 and 8-11 are pending in the application.

Claims 1-6 and 8 have been amended in accordance with the requirements of U.S. patent practice. New claims 9-11 add no new matter, as these claims contain subject matter deleted from the amended claims. Applicants respectfully request entry of the preliminary amendment.

Respectfully Submitted,

Michael F. Morgan Registration No. 42,906 Cusomer No. 26922

Date: June 26, 2001 BASF Corporation 26701 Telegraph Road Southfield, Michigan 48034-2442 (248)-948-2355

# WELTORGANISATION FÜR GEISTIGES EIGENTUM

Internationales Büro INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) (51) Internationale Patentklassifikation 7 -(11) Internationale Veröffentlichungsnummer: WO 00/46265

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C08G 18/08. 18/12, 18/32, 18/66, 18/72,

C09D 175/06

A1

(21) Internationales Aktenzeichen:

(43) Internationales Veröffentlichungsdatum:

10. August 2000 (10,08,00)

PCT/EP00/00779

(81) Bestimmungsstaaten: BR, JP, US, curopäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,

(22) Internationales Anmeldedatum: 1. Februar 2000 (01.02.00)

(30) Prioritätsdaten:

199 04 170 9 199 04 624.7

3. Februar 1999 (03.02.99) 5. Februar 1999 (05.02.99)

MC, NL, PT, SE). Veröffentlicht

Mit internationalem Recherchenbericht.

(71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF COATINGS AG [DE/DE]; Glasuritstr. 1, D-48165 Münster

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Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen

(74) Anwalt: FITZNER, Uwe; Lintorfer Str. 10, D-40878 Ratingen

454) Title: POLYURETHANE AND ITS USE IN AQUEOUS PAINTING PLASTIC

(54) Bezeichnung: POLYURETHAN UND SEINE VERWENDUNG IN DER WÄSSRIGEN KUNSTSTOFFLACKIERUNG

(57) Abstract

The invention relates to a polyurethane with a number average molecular weight Mn of 3,000 to 50,000 and an acid number of 10 to 35. Said polyurethane is produced by reacting (a1) at least one polyesterpolyol with a number average molecular weight Mn of 1,000 to 4,000, preferably 1,200 to 3,000, an acid number of 0 to 15, preferably 0 to 10, and an OH number of 35 to 150, preferably 50 to 120, on the basis of acyclic aliphatic and cycloaliphatic dicarbonic acids, (a2) a mixture of at least one diol and one triol, (a3) at least one compound having at least two functional groups (a31) that are reactive with isocyanate and at least one functional group (a32) that is capable of forming anions, and (a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate. The result of said reaction is a prepolymer that contains isocyanate groups. The prepolymer is subjected to a chain extension reaction with a multifunctional amine or amine alcohol and is optionally neutralized. The invention also relates to the use of said polyurethane for producing polyurethane dispersions and coating substances for painting plastic.

#### (57) Zusammenfassung

Polyurethan eines zahlenmittleren Molekulargewichts Mn von 3.000 bis 50.000 und einer Säurezahl von 10 bis 35 gefunden, welches herstellbar ist, indem man (a1) mindestens ein Polyesterpolyol eines zahlenmittleren Molekulargewichts Mn von 1,000 bis 4,000, vorzugsweise 1.200 bis 3.000, einer Säurezahl von 0 bis 15, vorzugsweise 0 bis 10, und einer OH-Zahl von 35 bis 150, vorzugsweise 50 bis 120, auf der Basis acyclischer aliphatischer und cycloaliphatischer Dicarbonsäuren; (a2) ein Gemisch aus mindestens einem Diol und einem Triol; (a3) mindestens eine Verbindung, welche mindestens zwei mit Isocyanat reaktive funktionelle Gruppen (a31) und mindestens eine zur Anionenbildung befähigte funktionelle Grupppe (a32) aufweist, und (a4) ein Gemisch aus mindestens einem acyclischen aliphatischen und mindestens einem cycloaliphatischen Diisocyanat zu einem isocyanatgruppenhaltigen Präpolymer umsetzt, wonach man das Präpolymer mit einem multifunktionellen Amin oder Aminoalkohol kettenverlängert und gegebenenfalls neutralisiert; sowie die Verwendung des Polyurethans zur Hetstellung von Polyurethandispersionen und Beschichtungsstoffen für die Kunststofflackierung.

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PAT 99 102 PCT

12.01.2000

EP-A-0 297 576,

EP-A-0 649 865,

## Polyurethane and its use in aqueous plastics finishing

The present invention relates to a novel polyurethane and to a novel polyurethane dispersion and to the use thereof in the aqueous finishing of plastics. The present invention additionally relates to a novel aqueous coating material which comprises the novel polyurethane and the novel polyurethane dispersion. The present invention further relates to a novel process for producing multicoat finishes on plastics. The present invention relates not least to novel finishes, including multicoat finishes, for plastics, and to plastics components which have these novel finishes.

15 Polyurethanes, their aqueous dispersions, agueous coating materials based on polyurethanes, the use of these aqueous coating materials as waterborne basecoat materials for producing multicoat finishes, by the weton-wet technique, for example, and also the finishes 20 themselves are known from the patents EP-A-0 089 497, EP-A-0 256 540,

WO 96/12747, EP-A-0 523 610, EP-A-0 228 003. EP-A-0 397 806. EP-A-0 574 417, EP-A-0 531 510, EP-A-0 581 211. EP-A-0 708 788, EP-A-0 593 454, DE-A-43 28 092, EP-A-0 299 148. EP-A-0 394 737. EP-A-0 590 484, EP-A-0 234 362, EP-A-0 234 361. EP-A-0 543 817, WO 95/14721, EP-A-0 521 928. EP-A-0 522 420.

EP-A-0 522 419.

EP-A-0 260 447,

EP-A-0 536 712, EP-A-0 596 460, EP-A-0 596 461, EP-A-0 584 818, EP-A-0 669 356, EP-A-0 634 431, EP-A-0 678 536, EP-A-0 354 261, EP-A-0 424 705,

WO 97/49745, WO 97/49747 and EP-A-0 401 565.

In automotive OEM finishing, these known aqueous coating materials and processes are outstandingly suitable for the wet-on-wet finishing of metal components coated beforehand with electrocoat materials and primer-surfacers or primers. In the wet-on-wet technique, as is known, the waterborne basecoat material is applied but then is not cured but instead is merely dried. The clearcoat material, in solution in organic solvents, is applied to the waterborne basecoat film, after which the two films are baked together.

Aqueous coating materials for the finishing of plastics are likewise known. They utilize the polyurethane dispersions of the known waterborne basecoat materials, which are described, inter alia, in the patents mentioned above. The plastics finishes in question, however, exhibit considerable weaknesses in moisture resistance. This becomes particularly evident in the condensation test and in the course of steam jet testing. These weaknesses are manifested in a particularly disadvantageous fashion on modern automobile bodies, where finished plastics components and metal components adjoin one another, since it is

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here that the difference in adhesion is especially pronounced.

It is an object of the present invention to provide a novel polyurethane and a novel polyurethane dispersion which no longer have the disadvantages of the prior art but which instead permit the preparation of aqueous coating materials which can be used for aqueous plastics finishing and provide single-coat or multicoat plastics finishes having outstanding optical properties and outstanding adhesion even following condensation exposure. Moreover, the novel aqueous coating materials should also be easy to apply by the wet-on-wet technique.

- 15 The invention accordingly provides the novel polyurethane which has a number average molecular weight Mn of from 3,000 to 50,000 and an acid number of from 10 to 35 and is preparable by reacting
- 20 (a1) at least one polyesterpolyol having a number average molecular weight Mn of from 1,000 to 4,000, preferably from 1,200 to 3,000, an acid number of from 0 to 15, preferably from 0 to 10, and an OH number of from 35 to 150, preferably from 50 to 120, based on acyclic aliphatic and cycloaliphatic dicarboxylic acids.
  - (a2) a mixture of at least one diol and one triol,

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- (a3) at least one compound containing at least two isocyanate-reactive functional groups (a31) and at least one functional group (a32) capable of forming anions, an
- (a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate,
- 10 with the proviso that
  - (i) in the mixture (a2) the diols and triols are in a molar ratio of from 2 : 1 to 13 : 1, preferably from 2.5 : 1 to 8 : 1,

(ii) the molar ratio of the polyesterpolyols (al) to the mixture (a2) is from 4.5 : 1 to 1 : 1, preferably from 3.5 : 1 to 1.5 : 1, and

- 20 (iii) in the mixture (a4) the acyclic aliphatic and cycloaliphatic diisocyanates are in a molar ratio of from 1 : 0.16 to 1 : 6, preferably from 1 : 0.5 to 1 : 5.5;
- 25 to give an isocyanato-containing prepolymer which is then chain extended with a polyfunctional amine or amino alcohol and, if desired, is neutralized.

In the text below, the novel polyurethane is referred to, for the sake of clarity, as the "polyurethane of the invention".

- 5 The invention additionally provides the novel polyurethane dispersion which comprises at least one polyurethane (A) of the invention dispersed in an aqueous medium (B).
- 10 In the text below, the novel polyurethane dispersion is referred to, for the sake of clarity, as the "polyurethane dispersion of the invention".
- The invention also provides the novel aqueous coating 15 materials which comprise at least one polyurethane (A) of the invention or one polyurethane dispersion (A/B) of the invention.

In the text below, the novel aqueous coating materials 20 are referred to, for the sake of clarity, as "coating materials of the invention".

The invention also provides a novel process for coating plastics with a multicoat finish by

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 applying a two component waterbased primer and curing it to give a primer coat,

- (II) applying an aqueous coating material to the primer coat,
- (III) applying a two component clearcoat material wet

  on wet, and
  - (IV) curing the resultant basecoat/clearcoat film,

using an aqueous coating material comprising

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- (A) at least one polyurethane preparable by reacting
  - (a1) a polyesterpolyol based on acyclic aliphatic and cycloaliphatic dicarboxylic acids,
  - (a2) a mixture of at least one diol and at least one triol,

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(a3) at least one compound containing at least two isocyanate-reactive functional groups (a31) and at least one functional group (a32) capable of forming anions, and

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(a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate

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to give an isocyanato-containing prepolymer which is then chain extended with a polyfunctional amine or amino alcohol and, if desired, is neutralized.

5 In the text below, the novel process for coating plastics with a multicoat finish is referred to, for the sake of brevity, as the "process of the invention".

The invention additionally provides the novel plastics finishes producible by means of the coating materials of the invention and/or with the aid of the process of the invention.

In the text below, the novel plastics finishes are referred to, for the sake of clarity, as the "plastics finishes of the invention".

The invention provides not least the novel plastics components which carry the plastics finishes of the invention and which are referred to below as "plastics components of the invention".

The polyurethane of the invention has a number average molecular weight Mn of from 3,000 to 50,000 and an acid number of from 10 to 35. It may be prepared by reacting the inventively suitable components described below with one another in the manner described below.

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The first important component for preparing the polyurethane of the invention is at least one polyesterpolyol (al) having a number average molecular weight Mn of from 1,000 to 4,000, preferably from 1,200 to 3,000, an acid number of from 0 to 15, preferably from 0 to 10, and an OH number of from 35 to 150, preferably from 50 to 120, based on acyclic aliphatic and cycloaliphatic dicarboxylic acids.

Examples of suitable acyclic aliphatic dicarboxylic acids for use in accordance with the invention are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedicarboxylic acid or dodecanedicarboxylic acid, of which adipic acid, glutaric acid, azelaic acid and/or sebacic acid are advantageous and are therefore used with preference.

Examples of suitable cycloaliphatic dicarboxylic acids used in accordance with the invention are 1,2-20 cyclobutanedicarboxylic acid, 1,3-cyclobutanedicarboxylic acid, 1,2-cyclopentanedicarboxylic acid, 1,3-cyclopentanedicarboxylic acid, hexahydrophthalic 1,3-cyclohexanedicarboxylic acid. 1,4-25 cyclohexanedicarboxylic acid, 4-methylhexahydrophthalic acid. and tricyclodecanedicarboxylic acid. The cycloaliphatic dicarboxylic acids may be used in both their cis form and their trans form and also as a mixture of both forms.

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Also suitable in accordance with the invention are the esterifiable derivatives of the abovementioned dicarboxylic acids, such as, for example, their monoesters or polyesters with aliphatic alcohols having from 1 to 4 carbon atoms or hydroxy alcohols having from 1 to 4 carbon atoms. It is also possible, moreover, to use the anhydrides of the abovementioned dicarboxylic acids, where they exist.

- 10 To prepare the polyesterpolyol (a1) the abovementioned dicarboxylic acids are reacted with diols and triols, especially diols. Examples of suitable diols and triols are those described below.
- The polyesterpolyol (a1) is prepared by the known methods of esterification, as described for example in DE-A-40 24 204, page 4 lines 50 to 65. The reaction normally takes place at temperatures between 180 and 280°C, in the presence, if desired, of an appropriate esterification catalyst, such as lithium octoate, dibutyltin oxide, dibutyltin dilaurate or paratoluenesulfonic acid, for example.

The polyesterpolyol (a1) is normally prepared in the
presence of small amounts of an appropriate azeotropeforming solvent. Examples of azeotrope formers used
include aromatic hydrocarbons, such as xylene in
particular, and (cyclo)aliphatic hydrocarbons, e.g.
cyclohexane or methylcyclohexane.

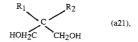
The second important component for preparing the polyurethane of the invention is a mixture (a2) of at least one diol and at least one triol.

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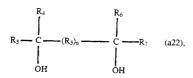
Suitable diols (a2) are ethylene glycol, 1,2- or 1,3- propanediol, 1,2-, 1.3- or 1,4-butanediol, 1,2-, 1,3-, 1,4- or 1,5-pentanediol, 1,2-, 1,3-, 1,4-, 1,5- or 1,6-hexanediol, neopentyl hydroxypivalate, neopentyl glycol, diethylene glycol, 1,2-, 1,3- or 1,4-cyclohexanediol, 1,2-, 1,3- or 1,4-cyclohexanediol, trimethylpentanediol, ethylbutylpropanediol or the positionally isomeric diethyloctanediols.

15 Further examples of suitable diols (a2) are diols of the formula (a21) or (a22)



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in which  $R_1$  and  $R_2$  each represent an identical or different radical and stand for an alkyl radical having from 1 to 18 carbon atoms, an aryl radical or a cycloaliphatic radical, with the proviso that  $R_1$  and/or  $R_2$  must not be methyl;



in which  $R_3$ ,  $R_4$ ,  $R_6$  and  $R_7$  each represent identical or different radicals and stand for an alkyl radical having from 1 to 6 carbon atoms, a cycloalkyl radical or an aryl radical and  $R_5$  represents an alkyl radical having from 1 to 6 carbon atoms, an aryl radical or an unsaturated alkyl radical having from 1 to 6 carbon atoms, and n is either 0 or 1.

Suitable diols (a21) include all propanediols of the formula (a21) in which either  $R_1$  or  $R_2$  or  $R_1$  and  $R_2$  is or are other than methyl, such as 2-butyl-2-ethyl-1,3-propanediol, 2-butyl-2-metyl-1,3-propanediol, 2-phenyl-2-methyl-1,3-propanediol, 2-propyl-2-ethyl-1,3-propanediol, 2-di-tert-butyl-1,3-propanediol, 2-butyl-2-propyl-1,3-propanediol, 1-dihydroxymethylbicyclo-[2.2.1]heptane, 2,2-diethyl-1,3-propanediol, 2,2-dipropyl-1,3-propanediol or 2-cyclohexyl-2-methyl-1,3-propanediol et cetera.

As diols (a22) (formula a22)) it is possible, for example, to use 2,5-dimethyl-2,5-hexanediol, 2,5-diethyl-2,5-hexanediol, 2-ethyl-5-methyl-2,5-hexanediol, 2,4-dimethyl-2,4-pentanediol, 2,3-dimethyl-2,3-

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butanediol, 1,4-bis(2'-hydroxypropy1)benzene and 1,3-bis(2'-hydroxypropy1)benzene.

Examples of suitable triols (a2) are trimethylolethane, 5 trimethylolpropane and glycerol, especially trimethylolpropane.

The third important component for preparing the polyurethane of the invention is at least one compound containing at least two isocyanate-reactive functional groups (a31) and at least one functional group (a32) capable of forming anions.

Suitable isocyanate-reactive functional groups (a31) are, in particular, hydroxyl groups and also primary and/or secondary amino groups, of which hydroxyl groups are advantageous and are therefore used with preference. Functional groups (a32) capable of forming anions are carboxyl, sulfonic acid and/or phosphonic acid groups, of which the carboxyl groups advantageous and are therefore used with preference. It preferred to use alkanoic acids having two substituents on the alpha carbon atom. The substituent may be a hydroxyl group, an alkyl group or an alkylol group. These polyols have at least one, generally from 1 to 3, carboxyl groups per molecule. Examples of suitable compounds (a3) are dimethylolpropionic acid, dimethylolpropanesulfonic acid or dimethylolpropanephosphonic acid, especially dimethylolpropionic acid.

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In general, compounds (a3) are used in an amount which renders the polyurethanes - generally incompatible with water - dispersible in water following neutralization with the amines or amino alcohols described below. Advantageously, the compounds (a3) are used in an amount which gives an acid number of from 10 to 35 mg KOH/g in the unneutralized prepolymer.

The fourth important component for preparing the polyurethane of the invention is a mixture (a4) of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate. In the context of the present invention, the term "cycloaliphatic diisocyanate" refers to a diisocyanate in which at least one isocyanate group is attached to a cycloaliphatic radical.

Examples of suitable cycloaliphatic diisocyanates (a4) for use in accordance with the invention are isophorone 20 diisocyanate (i.e., 5-isocyanato-1-isocyanatomethyl-1,3,3-trimethylcyclohexane), 5-isocyanato-1-(2-isocyanatoeth-1-y1)-1,3,3-trimethylcyclohexane, 5-isocyanato-1-(3-isocyanatoprop-1-yl)-1,3,3-trimethylcyclohexane. 5-isocyanato-(4-isocyanatobut-1-y1)-1,3,3trimethylcyclohexane, 1-isocyanato-2-(3-isocyanatoprop-25 1-yl)cyclohexane, 1-isocyanato-2-(3-isocyanatoeth-1yl)cyclohexane, 1-isocyanato-2-(4-isocyanatobut-1-yl)cyclohexane, 1,2-diisocyanatocyclobutane, diisocyanatocyclobutane, 1,2-diisocyanatocyclopentane,

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1,3-diisocyanatocyclopentane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatocyclohexane, dicyclohexylmethane 2,4'-diisocyanate or dicyclohexylmethane 4,4'-diisocyanate, especially isophorone diisocyanate.

Examples of suitable acyclic aliphatic diisocyanates in accordance with the invention trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene cyanate, ethylethylene diisocyanate, trimethylhexane diisocyanate, heptamethylene diisocyanate or diisocyanates derived from dimer fatty acids, as sold under the commercial designation DDI 1410 by Henkel and described in the patents WO 97/49745 and WO 97/49747, especially 2-heptyl-3, 4-bis(9-isocyanatononyl)-1pentylcyclohexane, or 1,2-, 1,4- or 1,3-bis(isocyanatomethyl)cyclohexane, 1,2-, 1,4- or 1,3-bis(2isocyanatoeth-1-yl)cyclohexane, 1,3-bis(3-isocyanatoprop-1-yl)cyclohexane or 1,2-, 1,4- or 1,3-bis(4isocyanatobut-1-yl)cyclohexane. The latter are counted among the acyclic aliphatic diisocyanates for the purposes of the present invention, owing to their two isocyanate groups attached exclusively to alkyl groups, and despite their cyclic groups. Of these diisocyanates, hexamethylene diisocyanate is advantageous in accordance with the invention and is therefore used with particular preference.

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In accordance with the invention, the above-described important components (a1), (a2), (a3), and (a4) are reacted with one another with the proviso that

- 5 (i) in the mixture (a2) the diols and the triols are in a molar ratio of from 2:1 to 13:1, preferably from 2.5:1 to 8:1,
  - (ii) the molar ratio of the polyesterpolyols (a1) to the mixture (a2) is from 4.5 : 1 to 1 : 1, preferably from 3.5 : 1 to 1.5 : 1, and
  - (iii) in the mixture (a4) the acyclic aliphatic and cycloaliphatic diisocyanates are in a molar ratio of from 1 : 0.16 to 1 : 6, in particular from 1 : 0.5 to 1 : 5.5.

In this context, the above-described important components (a1), (a2), (a3), and (a4) are reacted with one another in a ratio such as to give, in accordance with the invention, an isocyanato-containing prepolymer.

The reaction of components (a1), (a2), (a3), and (a4)

25 takes place in accordance with the well-known methods
of organic chemistry (cf., e.g., Kunststoff-Handbuch,
Volume 7: Polyurethane, edited by Dr. Y. Oertel, Carl
Hanser Verlag, Munich, Vienna 1983). Examples of the

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preparation of the prepolymers is described in DE-A-26 24 442 and DE-A-32 10 051.

The reaction of the components takes place, if desired, in ethoxyethyl propionate (EEP) as solvent. The amount of EEP may vary within wide limits and should be sufficient to form a prepolymer solution of appropriate viscosity. Generally speaking use is made of up to 70% by weight, preferably from 5 to 50% by weight, with particular preference less than 20% by weight, of solvent, based on the solids. Accordingly, for example, the reaction may be conducted with very particular preference at a solvent content of 10 - 15% by weight EEP, based on the solids.

If desired, components (a1), (a2), (a3), and (a4) may be reacted in the presence of a catalyst, such as organotin compounds and/or tertiary amines.

- 20 To prepare the prepolymers, the amounts of the components are chosen such that the equivalents ratio of NCO to OH groups is between 2.0 : 1.0 and >1.0 : 1.0, preferably between 1.4 : 1 and 1.1 : 1.
- 25 The NCO prepolymer contains at least approximately 0.5% by weight of isocyanate groups, preferably at least 1% by weight NCO, based on the solids. The upper limit is approximately 15% by weight, preferably 10% by weight, with particular preference 5% by weight NCO.

The isocyanate groups of the isocyanato-containing prepolymer are reacted with a modifier or chain extender. The modifier is preferably added in an amount such that chain extensions and hence increases in molecular weight occur. Modifiers used in accordance with the invention are organic compounds containing secondary and/or primary amino groups and also, if desired, hydroxyl groups, especially amino alcohols and/or polyamines having a functionality of two, three and/or more. Examples of suitable polyamines are ethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, and diethylenetriamine. Examples of suitable amino alcohols are ethanolamine, propanolamine, diethanolamine, and dipropanolamine. The polyamines and/or amino alcohols may also be used to neutralize the carboxylic, sulfonic and/or phosphonic acid groups incorporated into the prepolymer.

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The resultant polyurethane of the invention is neutralized if desired, provided this has not yet taken place by means of the amino alcohols and/or amines described above. Examples of suitable neutralizing agents are ammonia, ammonium salts, such as ammonium carbonate or ammonium hydrogen carbonate, for example, and also tertiary amines, such as trimethylamine, triethylamine, tributylamine, dimethylaniline, diethylaniline or triphenylamine, and/or amino alcohols such

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as dimethylethanolamine, diethylethanolamine, methyldiethanolamine or triethanolamine. Neutralization may take place in organic phase or in aqueous phase. Dimethylethanolamine is used with preference as neutralizing agent.

In accordance with the invention, the polyurethane of the invention is dispersed in an aqueous medium (B).

The aqueous medium (B) contains substantially water. The aqueous medium here may contain minor amounts of organic solvents such as ethoxyethyl propionate, butyl glycol and/or methyl ethyl ketone, the above-described neutralizing agents, the below-described crosslinking agents and/or coating additives (D) and/or other dissolved solid, liquid or gaseous, organic and/or inorganic substances of low and/or high molecular mass. In the context of the present invention, the term "minor amounts" means an amount which does not take away the aqueous character of the aqueous medium.

Alternatively, the aqueous medium (B) may comprise water alone.

25 The polyurethane dispersion (A/B) of the invention may be put to numerous end uses. It is especially suitable for use in the finishing of plastics, especially in the form of the coating material of the invention.

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The coating material of the invention advantageously comprises a basecoat material.

The coating material of the invention comprises color and/or effect pigments (C) in customary and known amounts. The pigments may comprise organic or inorganic compounds and may provide effect and/or color. On the basis of this large number of suitable pigments, therefore, the coating material of the invention ensures universal scope for use of the coating materials and makes it possible to realise a large number of shades and optical effects.

Effect pigments (C) which can be used include metal flake pigments such as commercially customary aluminum bronzes, aluminum bronzes chromated in accordance with DE-A-36 36 183, and commercially customary stainless steel bronzes, and also nonmetallic effect pigments, such as pearlescent pigments and interference pigments for example. Examples of suitable inorganic color pigments (C) are titanium dioxide, iron oxides, Sicotrans yellow, and carbon black. Examples of suitable organic color pigments are indanthrene blue, Cromophthal red, Irgazine orange, and Heliogen green.

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The coating material of the invention may further comprise customary and known, effective amounts of organic and inorganic fillers (C). Examples of suitable fillers are chalk, calcium sulfates, barium sulfate,

silicates such as talc or kaolin, silicas, oxides such aluminum hydroxide or magnesium hydroxide, as nanoparticles or organic fillers such as textile fibers, cellulose fibers, polyethylene fibers or wood flour

The coating material of the invention further comprises coatings additives (D) in customary and known, effective amounts.

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Examples of suitable coatings additives (D) are UV absorber; free radical scavengers; crosslinking catalysts, especially organometallic compounds, preferably organotin and/or organobismuth compounds or tertiary amines; slip additives; polymerization inhibitors; defoamers; adhesion promoters; leveling agents or film formation auxiliaries, e.g., cellulose derivatives.

As coatings additive (D) it is possible in particular

to use at least one rheology control additive. Examples

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of suitable rheology control additives (D) are those known from the patents WO 94/22968, EP-A-0 276 501, EP-A-0 249 201 and WO 97/12945; crosslinked polymeric 25 microparticles, as disclosed for example EP-A-0 008 127; inorganic phyllosilicates such aluminum magnesium silicates, sodium magnesium phyllosilicates and sodium magnesium fluorine lithium phyllosilicates of the montmorillonite type; silicas

such as Aerosils; or synthetic polymers containing ionic and/or associative groups, such as polyvinyl alcohol, poly(meth)acrylamide, poly(meth)acrylic acid, polyvinylpyrrolidone, styrene-maleic anhydride or ethylene maleic anhydride copolymers and their derivatives or hydrophobically modified ethoxylated urethanes or polyacrylates. As rheology control additives (D) it is preferred to use polyurethanes and/or phyllosilicates.

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Where the coating material of the invention is employed as a two component system, a customary and known polyisocyanate crosslinking agent is added to it prior to application.

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Examples of suitable crosslinking agents of this kind are, in particular, those known as paint polyisocyanates, containing free isocyanate groups attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic moieties. It is preferred to use polyisocyanates containing from 2 to 5 isocyanate groups per molecule and having viscosities of from 100 to 10,000, preferably from 100 to 5000, and - where manual mixing of the constituents of the coating material is envisaged - in particular from 500 to 2000 mPas 23°C). If desired, small amounts of organic solvent, preferably from 1 to 25% by weight based polyisocyanate alone, may be added to the polyisocyanates in order to improve the ease

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incorporation of the isocyanate and, where appropriate, to lower the viscosity of the polyisocyanate to a level within the abovementioned ranges. Examples of suitable solvent additives for the polyisocyanates are ethoxyethyl propionate, amyl methyl ketone, and butyl acetate. Moreover, the polyisocyanates may have undergone conventional hydrophilic or hydrophobic modification.

Examples of suitable isocyanates are, for example, described in "Methoden der organischen Chemie", Houben-Weyl, Volume 14/2, 4<sup>th</sup> edition, Georg Thieme Verlag, Stuttgart 1963, pages 61 to 70 and by W. Siefken, Liebigs Annalen der Chemie, Volume 562, pages 75 to 136. Examples of those suitable are the isocyanates mentioned in connection with the description of the polyurethane of the invention, and/or isocyanato-containing prepolymers which can be prepared by reacting polyols with an excess of polyisocyanates and which are preferably of low viscosity.

Further examples of suitable polyisocyanates are polyisocyanates containing isocyanurate, biuret, allophanate, iminooxadiazinedione, urethane, urea and/or uretdione groups. Polyisocyanates containing urethane groups, for example, are obtained by reacting some of the isocyanate groups with polyols, such as trimethylolopropane and glycerol, for example. It is preferred to use aliphatic or cycloaliphatic

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polyisocyanates, especially hexamethylene diisocyanate, dimerized and trimerized hexamethylene diisocyanate, isophorone diisocyanate, 2-isocyanatopropylcyclohexyl isocvanate. dicyclohexylmethane 2,4'-diisocyanate, dicyclohexylmethane 4,4'-diisocyanate, 1,3-bis-(isocyanatomethyl)cyclohexane, diisocyanates derived from dimer fatty acids, as sold under the commercial designation DDI 1410 by Henkel, 1,8-diisocyanato-4isocyanatomethyloctane, 1,7-diisocyanato-4-isocyanatomethylheptane 1-isocyanato-2-(3-isocyanatoor propyl)cyclohexane or mixtures of these polyisocyanates.

Very particular preference is given to using mixtures of polyisocyanates which contain uretdione and/or isocyanurate and/or allophanate groups and are based on hexamethylene diisocyanate, such mixtures being as formed by catalytic oligomerization of hexamethylene diisocyanate using appropriate catalysts. Moreover, the polyisocyanate constituent may also comprise any desired mixtures of the free polyisocyanates given by way of example.

Where necessary, the coating material of the invention
is adjusted to the appropriate application viscosity
using deionized water. It may be applied using the
customary and known application methods, such as
spraying, knife coating, brushing, flow coating,
dipping or rolling, for example, to any desired

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substrates, such as metal, wood, plastic, glass or paper, for example, but especially plastic.

The coating material of the invention is outstandingly suitable in particular for the process of the invention.

The process of the invention is used to coat plastics with a multicoat finish.

The process starts in step (I) with the application and curing of a two component waterbased primer to give a primer coat. Suitable waterbased primers in this context are the customary and known, commercially available primers for plastics.

In step (II) of the process, an aqueous coating material is applied to the primer coat. In accordance with the invention the aqueous coating material used here is one which

- (A) comprises at least one polyurethane preparable by reacting
- 25 (a1) a polyesterpolyol based on acyclic aliphatic and cycloaliphatic dicarboxylic acids,
  - (a2) a mixture of at least one diol and at least one triol,

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- (a3) at least one compound containing at least two isocyanate-reactive functional groups (a31) and at least one functional group (a32) capable of forming anions, and
- (a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate
- 10 to give an isocyanato-containing prepolymer which is then chain extended with a polyfunctional amine and/or amino alcohol and, if desired, is neutralized.
  - For the process of the invention it is of advantage if the polyurethane (A) is in dispersion in an aqueous medium (B).

Examples of polyurethanes (A) and polyurethane dispersions (A/B) which are outstandingly suitable for the process of the invention are the polyurethanes and polyurethane dispersions of the invention described in detail above.

In accordance with the invention, the applied coating material is merely dried, but not completely cured.

In step (III) of the process, a two component clearcoat material is applied wet-on-wet to the basecoat film applied in step (II) of the process. In this step it is

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possible to employ the clearcoat materials which are known from automotive refinish and which comprise binders containing isocyanate-reactive groups and the above-described polyisocyanates as crosslinking agents in solution or dispersion in organic solvents.

In accordance with the invention, in step (IV) of the process, the resultant basecoat/clearcoat film is cured to give the multicoat plastics finishes of the invention.

The plastics finish produced in accordance with the process of the invention and/or with the aid of the coating material of the invention is outstandingly suitable for coating all customary and known primed or unprimed plastics.

Examples of such plastics are ABS, AMMA, ASA, CA, CAB, EP, UF, CF, MF, MPF, PF, PAN, PA, PE, HDPE, LDPE, 20 LLDPE, UHMWPE, PET, PMMA, PP, PS, SB, PUR, PVC, RF, SAN, PBT, PPE, POM, PUR-RIM, SMC, BMC, PP-EPDM and UP (abbreviations to DIN 7728T1). The plastics to be coated may of course also be polymer blends, modified plastics or fiber reinforced plastics. It is also possible to employ plastics commonly used in vehicle construction especially motor vehicle construction.

Nonfunctionalized and/or nonpolar substrate surfaces are advantageously subjected prior to coating in a

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customary and known manner to a pretreatment, for instance by means of a plasma or by flaming.

The plastics finishes of the invention exhibit

outstanding adhesion between the layers and on the
plastics surface, even under extremely moist and hot
climatic conditions. The visual impression is
outstanding.

### 10 Inventive and comparative examples

#### Preparation Example 1

The preparation of the inventive polyurethane dispersion 1

animber average molecular weight Mm of 1819 and an acid number of 3.5 (prepared from 7.094 mol of adipic acid, 7.094 mol of hexahydrophthalic anhydride and 15.962 mol of hexanediol), 1559 parts by weight of methyl ethyl ketone and 80.4 parts by weight of trimethylolpropane, 88.4 parts by weight of neopentyl glycol, 504 parts by weight of hexamethylene diisocyanate and 666 parts by weight of isophorone diisocyanate were heated at 65°C under a nitrogen atmosphere in an appropriate reaction vessel, with stirring. The reaction was carried out until the NCO content was 1.0% by weight, based on the resin solids. Thereafter, 121.7 parts by weight of

diethanolamine were added, and the mixture was stirred at 65°C until free isocyanate groups were no longer detectable. The resultant polyurethane had an acid number of 21.

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Subsequently, 123.2 parts by weight of dimethylethanolamine and 1054 parts by weight of butyl glycol were added slowly with stirring, after which 11,185 parts by weight of deionized water were introduced slowly into the mixture. The methyl ethyl ketone was distilled off under reduced pressure.

The result was a fine dispersion whose pH was adjusted to 7.4 using dimethylethanolamine and whose nonvolatile fraction was adjusted to 27 percent using deionized water.

### Preparation Example 2

## 20 The preparation of the noninventive polyurethane dispersion 2

3562 parts by weight of a polyesterpolyol having a number average molecular weight Mn of 1819 and an acid 25 number of 3.5 (prepared from 1 mol of a dimer fatty acid with a dimer content of at least 98% by weight, a trimer content of not more than 2% by weight and a monomer content in the trace range, 1 mol of isophthalic acid and 2.626 mol of hexanediol), 2751

parts by weight of methyl ethyl ketone, 287 parts by weight of dimethylolpropionic acid, 44 parts by weight of neopentyl glycol and 1332 parts by weight of isophorone diisocyanate were heated at 80°C under a nitrogen atmosphere in an appropriate reaction vessel, with stirring. The reaction was carried out until the NCO content was 1.0% by weight, based on the resin solids. Thereafter, 184 parts by weiaht trimethylolpropane were added, and the mixture was stirred at 80°C until free isocyanate groups were no longer detectable. The resultant polyurethane had an acid number of 24.

Subsequently, 166 parts by weight of dimethylethanolamine and 1044 parts by weight of butyl glycol were added slowly with stirring, after which 11,574 parts by weight of deionized water were introduced slowly into the mixture. The methyl ethyl ketone was distilled off under reduced pressure.

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#### Preparation example 3

# The preparation of the noninventive polyurethane dispersion 3

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To prepare the noninventive polyurethane dispersion 3, Example 1.1 "binder dispersion A" described on page 9 of European patent EP-B-0 521 928 was repeated. The resultant, coagulum-free dispersion having a pH of 8.1

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was adjusted to a solids content of 27 percent using deionized water.

The result was a fine dispersion whose pH was adjusted to 7.4 using dimethylethanolamine and whose nonvolatile fraction was adjusted to 27 percent using deionized water.

#### Inventive example 1

Preparation of an inventive white solid-color waterborne basecoat material 1

42 parts by weight of the inventive polyurethane dispersion from Preparation example 1 were mixed in a dissolver for 15 minutes with 9 parts by weight of butyl glycol, 3.5 parts by weight of a commercially customary anionic dispersing aid, 0.5 part by weight of a commercially customary defoamer, 7 parts by weight of a commercial inorganic thickener (phyllosilicate; Laponite® from Laporte) and 31 parts by weight of titanium dioxide. The resultant mixture was dispersed in a bead mill to a particle size of 15 µm.

25 The pH of the solid-color waterborne basecoat material was subsequently adjusted to 8.0 using dimethylethanolamine. For application, the solid-color waterborne basecoat material was adjusted to a viscosity of 25 s in the DIN 4 cup using deionized water.

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### Inventive example 2

# The preparation of the inventive green solid-color waterborne basecoat material 2

50 parts by weight of the inventive polyurethane dispersion from Preparation example 1 were mixed in a dissolver for 15 minutes with 9 parts by weight of butyl glycol, 2.8 parts by weight of the commercially customary anionic dispersing aid, 0.5 part by weight of the commercially customary defoamer, 7 parts by weight of the commercial inorganic thickener, eight parts by weight of titanium dioxide and 04 part by weight of a commercially customary organic green pigment. The mixture was then dispersed in a bead mill to a particle size of 15  $\mu$ m.

The pH of the solid-color waterborne basecoat material was subsequently adjusted to 8.0 using dimethylethanolamine. For application, its viscosity was adjusted to 25 s in the DIN 4 cup using deionized water.

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#### Comparative examples C1 to C6

# The preparation of the noninventive waterborne basecoat materials C1 to C6

Inventive examples 1 and 2 were repeated but using, instead of the inventive polyurethane dispersion 1 from Preparation example 1,

- 10 for Comparative examples C1 and C2, a commercial polyurethane dispersion (Daotan® VTW 1237 from Vianova);
  - for Comparative examples C3 and C4, the noninventive polyurethane dispersion 3 from Preparation example 3; and
    - for Comparative examples C5 and C6, the noninventive polyurethane dispersion 2 from Preparation example 2.

Inventive examples 3 and 4 and Comparative examples C7 to C12

The preparation of inventive (Inventive examples 3 and 5 4) and noninventive (Comparative examples C7 to C12) plastics finishes

For Inventive example 3, the inventive waterborne basecoat material 1 from Inventive example 1 and, for Inventive example 4, the inventive waterborne basecoat material 2 from Inventive example 1 was used.

For Comparative examples C7 and C8, the waterborne basecoat materials from Comparative examples C1 and C2, respectively, were used.

For Comparative examples C9 and C10, the waterborne basecoat materials from Comparative examples C3 and C4, respectively, were used.

For Comparative examples C11 and C12, the waterborne basecoat materials from Comparative examples C5 and C6, respectively, were used.

25 The surface of plastics panels made from commercial polypropylene (PP) which is used in vehicle construction for the production of fenders (Daplen® from PCD) was flame treated using a propane gas flame and coated with a commercially customary two-component

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waterbased primer. The resultant primer coats had a thickness of from 15 to 20  $\mu m$  after drying at 60°C for 15 minutes. The waterborne basecoat materials of Inventive examples 1 and 2 and of Comparative examples C1 to C6 were applied to the primer coats using a gravity feed gun. Following a flashoff time of 10 minutes, a commercial component clearcoat material was applied. The resultant multicoat finishes were baked at 90°C for 30 minutes.

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All multicoat finishes were subjected to the following tests:

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T1: 668 hours of condensate water exposure to DIN 50017; assessment of the surface to DIN 53209.

T2: as P1; assessment of the adhesion to DIN 53151.

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T3: steam jet test (a circular jet nozzle with a water pressure of 80 bar and water temperature of 80°C was directed onto the test area, into which a St. Andrew's Cross had been scribed, at a distance of 10 cm for 2 minutes).

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The table gives an overview of the test results obtained.

Table: Test results

Inventive and		Tes	its
Comparative examples	T1	Т2	Т3
3	m0/g0	Gt 0	no flaking
4	m0/g0	Gt 0	no flaking
C7	m2/g1	Gt 0	1 mm flaking
C8	m1/g2	Gt 1	no flaking
C9	m3/g3	Gt 5	5 mm flaking
C10	m4/g3	Gt 5	no flaking
C11	m2/g2	Gt 2	no flaking
C12	m3/g2	Gt 3	2 mm flaking

The test results underline the superiority of the inventive finishes based on the inventive coating materials or inventive polyurethane dispersions 1 and 2 over the finishes based on the noninventive coating materials or noninventive polyurethane dispersions.

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#### What is claimed is:

- A polyurethane which has a number average molecular weight Mn of from 3,000 to 50,000 and an
   acid number of from 10 to 35 and is preparable by reacting
  - (a1) at least one polyesterpolyol having a number average molecular weight Mn of from 1,000 to 4,000, an acid number of from 0 to 15, and an OH number of from 35 to 150, based on acyclic aliphatic and cycloaliphatic dicarboxylic acids,
  - (a2) a mixture of at least one diol and one triol.
    - (a3) at least one compound containing at least
      two isocyanate-reactive functional groups
      (a31) and at least one functional group
      (a32) capable of forming anions, and
    - (a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate,

with the proviso that

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- (i) in the mixture (a2) the diols and triols are in a molar ratio of from 2 : 1 to 13 : 1,
- 5 (ii) the molar ratio of the polyesterpolyols  $(a1) \ \mbox{to the mixture (a2) is from } 4.5:1$  to 1:1, and
  - (iii) in the mixture (a4) the acyclic aliphatic and cycloaliphatic diisocyanates are in a molar ratio of from 1 : 0.16 to 1 : 6;

to give an isocyanato-containing prepolymer which is then chain extended with a polyfunctional amine or amino alcohol and, if desired, is neutralized.

- 2. A polyurethane dispersion comprising
- $\begin{tabular}{lll} \textbf{(A)} & at least one polyure than eas claimed in claim \\ 20 & 1 \end{tabular}$ 
  - (B) in dispersion in an aqueous medium.
- The use of the polyurethane as claimed in claim 1
   or the polyurethane dispersion as claimed in claim
   in plastics finishing.

- The use of the polyurethane as claimed in claim 1 or the polyurethane dispersion as claimed in claim 2 in an aqueous coating material.
- 5 5. The use of the polyurethane as claimed in claim 1 or the polyurethane dispersion as claimed in claim 2 in an aqueous coating material, said material further comprising color and/or effect pigments (C).

 The use of the polyurethane as claimed in claim 1 or the polyurethane dispersion as claimed in claim 2 in an aqueous coating material, said material further comprising coatings additives (D).

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The use of the polyurethane as claimed in claim 1
or the polyurethane dispersion as claimed in claim
2 in an aqueous coating material for plastics
finishing.

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8. The use of the polyurethane as claimed in claim 1 or the polyurethane dispersion as claimed in claim 2 in plastics finishing, wherein the plastics finish is obtained by the steps of

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 applying a two component waterbased primer and curing it to give a primer coat,

- (II) applying an aqueous coating material to the primer coat,
- (III) applying a two component clearcoat material wet on wet, and
  - (IV) curing the resultant basecoat/clearcoat film.

#### Polyurethane and its use in plastics finishing

#### Abstract

A polyurethane which has a number average molecular weight Mn of from 3,000 to 50,000 and an acid number of from 10 to 35 and is preparable by reacting

- (a1) at least one polyesterpolyol having a number average molecular weight Mn of from 1,000 to 4,000, preferably from 1,200 to 3,000, an acid number of from 0 to 15, preferably from 0 to 10, and an OH number of from 35 to 150, preferably from 50 to 120, based on acyclic aliphatic and cycloaliphatic dicarboxylic acids,
- (a2) a mixture of at least one diol and one triol,
- (a3) at least one compound containing at least two isocyanate-reactive functional groups (a31) and at least one functional group (a32) capable of forming anions, and
- (a4) a mixture of at least one acyclic aliphatic and at least one cycloaliphatic diisocyanate,

with the proviso that

- (i) in the mixture (a2) the diols and triols are in a molar ratio of from 2 : 1 to 13 : 1, preferably from 2.5 : 1 to 8 : 1,
- (ii) the molar ratio of the polyesterpolyols (a1) to the mixture (a2) is from 4.5:1 to 1:1, preferably from 3.5:1 to 1.5:1, and
- (iii) in the mixture (a4) the acyclic aliphatic and cycloaliphatic diisocyanates are in a molar ratio of from 1: 0.16 to 1: 6, preferably from 1: 0.5 to 1: 5.5:
- to give an isocyanato-containing prepolymer which is then chain extended with a polyfunctional amine or amino alcohol and, if desired, is neutralized; and the use of the polyurethane for preparing polyurethane dispersions and coating materials for the finishing of plastics.

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DECLARATION FOR UTILITY	/ OR	Attorney Dock	et No.	IN-5495
DESIGN		First Named In	ventor	Stephan SCHWARTE et al.
PATENT APPLICATION (37 CFR 1.63)			COMP	LETE IF KNOWN
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• .	surcharge	Filing Date		June 26, 2001
Filing (37 CF)	R 1.16 (e))	Group Art Unit	_	
require	d	Examiner Nam	ne l	
As below named inventor, I hereby declare that:				
My residence, post office address and citizenship	are as stated helow	nevt to my name		
I believe I am the original, first and sole inventor ( listed below) of the subject matter which is claims  POLYURETHANE AND ITS USE IN	if only name is listed d and for which a pa	below) or an originatent is sought on t	he invention	
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The specification of which:		,		
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Was filed on	as United State	s Application or P	CT Internati	onal Application Number
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acknowledge the duty to disclose information wto part applications, material information which becate the material film and the continuation-in-part	me available betwee			
hereby claim foreign priority benefits under 3 certificate or 365 (a) of any PCT international ag- fitsed below and have also identified below, by ch international application(s) having a filing date bef	oplication(s) designated ecking the box, any ore that of the application	iting at least one of foreign application ation on which price	country other (s) for pate ority is claim	er than the United States of America nt or inventor's certificate, or any PCT ned.
Prior Foreign Application Country Number(s)	Foreign Filing DATE/MONTH/Y			Certified Copy Attached? Yes No
199 04 170.9 Germany	3. February 1	999		
199 04 624.7 Germany	5. February 1	999		
Additional foreign application number	er are listed on a su	pplemental priority	data sheet	PTO/SB/02B attached hereto:
I hereby claim the benefit under 35			visional app	lication(s) listed below:
APPLICATION NUMBER(S)	FILING D	AIE	_	7 Additional analysis of a 200
				Additional provisional application
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Combined Declaration For Patent Application and Practitioner's Docket No. IN-5495 Power of Attorney (Continued) POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number). Anne Gerry Sabourin Registration No. 33.772 Anna M. Budde Registration No. 35.085 Mary E. Golota Registration No. 36,814 Michael P. Brennan Registration No. 30,612 Fernando A. Borrego Registration No. 34.780 Brian Steaman Registration No. 30,977 Karen M. Dellerman Registration No. 33.592 David Banchik Registration No 36,439 Barbara Maurer Registration No 31,278 Mark Westhafer Registration No 42,220 Charles Costello Registration No 27.324 David LaPrairie Registration No 46,295 Michael F. Morgan Registration No 42,906 Send Correspondence to: Direct Telephone Calls to: Direct Telephone Calls to: BASE CORPORATION (name and telephone number) (name and telephone number) PATENT DEPARTMENT Anne Gerry Sabourin Mary E. Golota 26701 TELEGRAPH ROAD (248) 948-2021 Fax (248) 948-(248) 948-2020 Fax (248) 948-SOUTHFIELD, MI 48034-2442 2093 2093 00 DECLARATION Dfi I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, to both, under Section 1001 of cities of the United States Code, and that such willful false statements may jeopardize the validity of the application.

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SIGNATU	RE OF INVENTOR 201	TYPED NAME	DATE

	d Declaration For Power of Attorne	r Patent Application and	Practitioner's Docket No. IN-5495
POWER OF ATTO	DRNEY: As a named inve	hereby appoint the following attorn emark Office connected therewith (List n	Ley(s) and/or agent(s) to prosecute this application and ame and registration number).
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